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Catalytic Enantioselective Arylation of *N*-Tosylarylimines with Arylboronic Acids Using C_2-Symmetric Cationic *N*-Heterocyclic Carbene Pd^{2+} Diaquo Complexes

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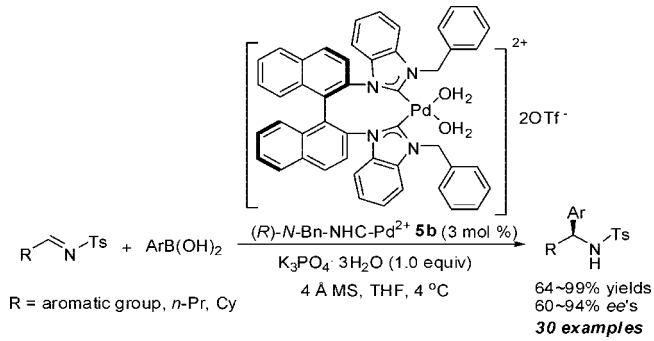
ABSTRACT



The asymmetric arylation of *N*-tosylimines with arylboronic acids was realized by using chiral cationic C_2-symmetric *N*-heterocyclic carbene (NHC) Pd^{2+} diaquo complex 5b as the catalyst in combination with 1.0 equiv of $K_3PO_4 \cdot 3H_2O$ in THF at 4 °C in the presence of powdered 4 Å MS to afford the corresponding adducts in excellent yields (up to 99%) and good to high enantioselectivities (up to 94% ee).

In the past decade, the use of *N*-heterocyclic carbenes (NHCs) as ligands for metal-mediated reactions has attracted considerable attention.[1] NHCs as the chiral ligands showed several advantages over their phosphine counterparts. Usually, NHC ligands are stronger σ donors and weaker π acceptors than phosphine ligands; these ligands are also air/moisture stable, which makes handling much more convenient. These advantages have attracted several research groups to search for new catalytic systems using NHCs as ancillary ligands for many catalytic reactions, such as NHC−Ru catalyzed olefin metathesis,[2a,b] transition-metal-mediated cross-coupling reactions,[2c−e] and transfer hydrogenation of ketones.[2f,g] Thus far, there have been few reports

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regarding the use of chiral NHC−metal complexes in asymmetric catalysis.[1c,3] In this paper, we report the first example of using chiral C_2-symmetric cationic NHC−Pd^{2+} diaquo complexes,[4] derived from 1,1′-binaphthalenyl-2,2′-diamine (BINAM) and H_8-BINAM, for the enantioselective arylation of *N*-tosylimines with arylboronic acids under mild conditions.[5−7]

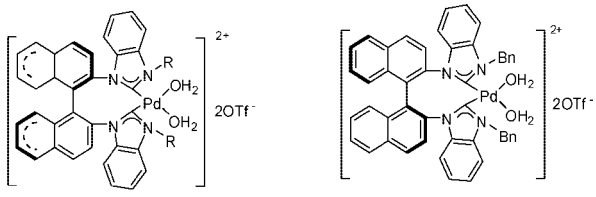

Figure 1. Chiral cationic NHC−Pd^{2+} diaquo complexes **5a**−**e**.

As shown in Figure 1, a series of the chiral cationic NHC−Pd^{2+} diaquo complexes **5a**−**e** were designed and synthesized in a three-step pathway starting from optically active 2,2′-di(1*H*-benzo[*d*]imidazol-1-yl)-1,1′-binaphthyl **1**. The corresponding imidazolium salts **3a**−**c** were afforded in good yields from the reaction of optically active (*R*)-**1** with alkyl halides **2a**−**c** (RX, X = Br, I) in dioxane under reflux, which were then converted to the NHC−PdX_2 complexes **4a**−**c** (X = Br, I) by treatment with $Pd(OAc)_2$. The cationic NHC−Pd(II) catalysts **5a**−**c** were prepared in quantitative yields by mixing NHC−PdX_2 complexes **4a**−**c** with 1.1 equiv of AgOTf in CH_2Cl_2 and CH_3CN. Similarly, NHC−Pd(II) complexes **5d** and **5e** were synthesized from (*S*)-**1** and (*R*)-H_8-**1** by the same procedures, respectively. The detailed reaction procedures as well as the spectroscopic data can be found in the Supporting Information. The crystalline catalyst, **5a**, was obtained and determined by X-ray structural analysis, and its ORTEP drawing is shown in Figure 2, and its CIF data are presented in the Supporting Information.[8]

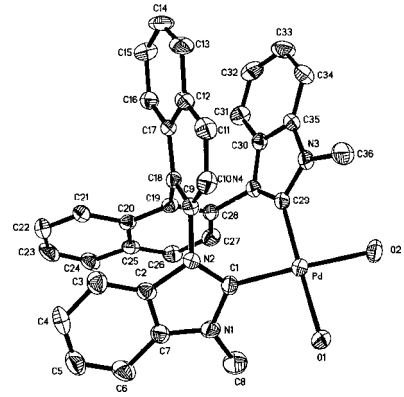

Figure 2. ORTEP drawing of NHC−Pd(II) complex **5a**. Thermal ellipsoids at the 30% probability level. Counterions (OTf-) and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−C1 = 1.940(5), Pd−C29 = 1.970(5), Pd−O1 = 2.094 (4), Pd−O2 = 2.102 (4), N2−C9 = 1.428 (6), N4−C28 = 1.449(6), O1−Pd−O2 = 90.73(18), C1−Pd−C29 = 92.3(2), C1−Pd−O1 = 88.5(2), C29−Pd−O2 = 88.7(2), O1−Pd−C29 = 175.9(2), C1−Pd−O2 = 179.2(2), N1−C1−N2 = 106.5(4), N3−C29−N4 = 107.8(4).

An initial experiment was carried out by reacting *N*-tosylimine **6a** with phenylboronic acid **7a** in the presence of NHC−Pd^{2+} diaqua catalyst **5a** (3 mol %) together with 4 Å molecular sieves. The reaction was conducted in anhydrous THF at 20 °C to afford **8aa** in 43% yield and 58% ee with the *S*-configuration for the major enantiomer. Adding 1.0 equiv of KOH or K_3PO_4•$3H_2O$ to the catalytic system led to product, **8aa**, in 82% yield/84% ee and 81% yield/80% ee, respectively (Table S1 in the Supporting Information).[9]

We next evaluated the cationic NHC−Pd^{2+} catalysts **5b**−**e** for the arylation of *N*-tosylimine **6a** with **7a** by using 1.0 equiv of KOH or K_3PO_4•$3H_2O$ as the base in various solvents under the standard conditions. The results of these experiments are summarized in Table 1 (Table S2 in the Supporting Information). Using **5b** as the catalyst produced **8aa** in >99%

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(6) Selected papers of Rh(I)-catalyzed asymmetric addition of *N*-tosylarylimines with arylboronic acids: (a) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shinatani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 13584. (b) Jagt, R. B. C.; Toullec, P. Y.; Geerdink, D.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2789. (c) Duan, H.; Jia, Y.; Wang, L.; Zhou, Q. *Org. Lett.* **2006**, *8*, 2567. (d) Wang, Z. Q.; Feng, C. G.; Xu, M. H.; Lin, G. Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336. (e) Chiara, M.; Chiara, M.; Cesare, G.; Umberto, P. *Synlett* **2007**, 2213. For Rh(I)-catalyzed asymmetric addition of *N*-Boc-arylimines (Boc = *tert*-butyloxycarbonyl) with arylboronic acids, see: (f) Nakagawa, H.; Rech, J. C.; Sindelar, R. W.; Ellman, J. A. *Org. Lett.* **2007**, *9*, 5155. For Rh(I)-catalyzed asymmetric addition of *N*-Dpp-arylimines (Dpp = diphenylphosphinoyl) with arylboronic acids, see: (g) Weix, D. J.; Shi, Y.; Ellman, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 1092. For selected papers of Pd(II)-catalyzed asymmetric addition of *N*-tosylarylimines with arylboronic acids, see: (h) He, P.; Lu, Y.; Hu, Q. S. *Tetrahedron Lett.* **2007**, *48*, 5283. (i) Zhang, Q.; Chen, J.; Wu, M.; Cheng, J.; Qin, C.; Su, W.; Ding, J. *Synlett* **2008**, 935.

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(8) The crystal data of **5a** have been deposited with the CCDC (no. 299484): empirical formula, $C_{38}H_{32}F_6N_4O_9PdS_2$; formula weight, 973.20; crystal color, habit, colorless, prismatic; crystal dimensions, 0.339 × 0.167 × 0.119 mm; crystal system, orthorhombic; lattice type, primitive; lattice parameters, a = 8.9946(5) Å, b = 19.7790(10) Å, c = 22.9386(12) Å, α = 90°, β = 90°, γ = 90°, V = 4080.6(4) Å^3; space group, $P2(1)$; Z = 4; D_{calc} = 1.584 g/cm^3; F_{000} = 1968; diffractometer, Rigaku AFC7R; residuals, R; wR, 0.0507, 0.0966.

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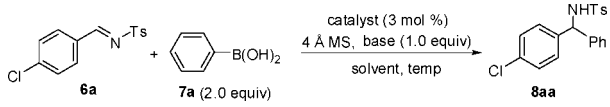
yield and 80% ee, which is more effective than **5c** and **5e** under the standard conditions (Table 1, entries 1, 2, and 4). Moreover, using **5d** as the catalyst afforded **8aa** in >99% yield and 82% ee with the *R*-configuration for the major enantiomer (Table 1, entry 3). The examination of the solvents using **5a** as the catalyst revealed that THF is the solvent of choice. In acetonitrile, the reaction became sluggish, and in DMF, no reaction occurred (Table 1, entries 5 and 19, 4 > 11). Upon examination of the reaction temperature, we found that carrying out the reaction at 4 °C provided **8aa** in 86% ee and 75% yield using **5a** as the catalyst after 36 h (Table 1, entries 12−15). Pleasingly, it was found that the use of NHC−Pd^{2+} diaqua catalyst **5b** as the catalyst and $K_3PO_4{\cdot}3H_2O$ as the base led to the adduct **8aa** in >99% yield and 90% ee in THF at 4 °C (Table 1, entry 17). In the presence of NHC−Pd^{2+} catalyst **5d**, adduct **8aa** was obtained in >99% yield and 88% ee with the *R*-configuration under identical conditions (Table 1, entry 18).

Having established an optimal reaction condition, the arylation of a variety of *N*-tosylimines **6b**−**r** having diverse substituents on the benzene rings was evaluated for the reaction with **7a**. The results are summarized in Table 2. The diarylmethyltosylamide products **8** were generated in high yields (up to 99%) and good ee's (up to 94%) whether they have electron-donating or electron-withdrawing substituents on their benzene rings. Furthermore, the position of substituents of imine substrates is not restrictive for obtaining high enantioselectivities (Table 2, entries 1−16). For *N*-tosyl heterocyclic imines **6q** and **6r**, the adducts **8qa** and **8ra** were obtained in 99% yield/80% ee and 87% yield/83% ee, respectively (Table 2, entries 17 and 18).

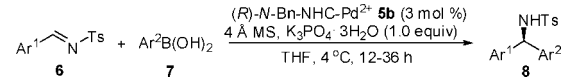
Table 1. Catalyst Screening and Reaction Condition Optimization[a]



entry	catalyst	base	solvent	*T* (°C)	time (h)	yield of **8aa**[b] (%)	ee of **8aa**[c] (%)
1	***5b***	***KOH***	***THF***	***20***	***12***	***>99***	***80 (S)***
2	**5c**	KOH	THF	20	36	20	77 (*S*)
3	***5d***	***KOH***	***THF***	***20***	***12***	***>99***	***82 (R)***
4	**5e**	KOH	THF	20	36	47	66 (*S*)
5	**5a**	KOH	toluene	20	36	83	11 (*S*)
6	**5a**	KOH	dioxane	20	36	82	40 (*S*)
7	**5a**	KOH	CH_2Cl_2	20	36	75	20 (*R*)
8	**5a**	KOH	$CHCl_3$	20	36	94	35 (*R*)
9	**5a**	KOH	MeOH	20	36	60	31 (*S*)
10	**5a**	KOH	CH_3CN	20	48	<10	n.d.
11	**5a**	KOH	DMF	20	36	n.r.	n.d.
12	**5a**	KOH	THF	4	36	75	86 (*S*)
13	**5a**	KOH	THF	−10	36	<10	n.d.
14	**5a**	KOH	THF	50	36	68	73 (*S*)
15	**5a**	KOH	THF	reflux	36	40	62 (*S*)
16	**5b**	KF	THF	4	12	>99	83 (*S*)
17	***5b***	***$K_3PO_4{\cdot}3H_2O$***	***THF***	***4***	***12***	***>99***	***90 (S)***
18	***5d***	***$K_3PO_4{\cdot}3H_2O$***	***THF***	***4***	***12***	***>99***	***88 (R)***
19	**5b**	KOH	THF	0	24	<99	83 (*S*)
20	**5b**	$K_3PO_4{\cdot}3H_2O$	THF	0	24	93	90 (*S*)

[a] Reaction conditions: phenylboronic acid (**7a**, 0.5 mmol), *N*-tosyl-*p*-chlorobenzaldehyde imine (**6a**, 0.25 mmol), NHC−Pd^{2+} (3 mol %, 0.0075 mmol), and 4 Å MS (200 mg). [b] Isolated yields. [c] The ee value was determined by HPLC using a Chiralcel OD-H column.

Table 2. Catalytic Asymmetric Arylation of *N*-Tosylimines **6** with Phenylboronic Acid **7aa**[a]



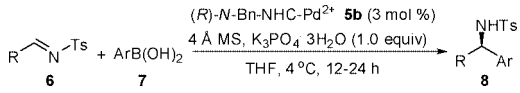
entry	Ar^1	Ar^2	yield of **8** (%)[b]	ee of **8** (%)[c,d]
1	4-ClC_6H_4 (**6a**)	C_6H_5 (**7a**)	99 (**8aa**)	90 (*S*)
2	3-ClC_6H_4 (**6b**)	C_6H_5 (**7a**)	97 (**8ba**)	82 (*S*)
3	2-ClC_6H_4 (**6c**)	C_6H_5 (**7a**)	99 (**8ca**)	90 (*S*)
4	4-BrC_6H_4 (**6d**)	C_6H_5 (**7a**)	64 (**8da**)	60 (*S*)
5	3-BrC_6H_4 (**6e**)	C_6H_5 (**7a**)	85 (**8ea**)	94 (*S*)
6	2-BrC_6H_3 (**6f**)	C_6H_5 (**7a**)	93 (**8ea**)	84 (*S*)
7	4-FC_6H_4 (**6g**)	C_6H_5 (**7a**)	99 (**8ga**)	94 (*S*)
8	2,4-$Cl_2C_6H_3$ (**6h**)	C_6H_5 (**7a**)	96 (**8ha**)	90 (*S*)
9	2,3-$Cl_2C_6H_3$ (**6i**)	C_6H_5 (**7a**)	96 (**8ia**)	86 (S)
10	4-$CH_3C_6H_4$ (**6j**)	C_6H_5 (**7a**)	99 (**8ja**)	90 (*S*)
11	4-$CH_3OC_6H_4$ (**6k**)	C_6H_5 (**7a**)	99 (**8ka**)	88 (*S*)
12	2-$CH_3OC_6H_4$ (**6l**)	C_6H_5 (**7a**)	99 (**8la**)	92 (*S*)
13	4-$NO_2C_6H_4$ (**6m**)	C_6H_5 (**7a**)	99 (**8ma**)	84 (*S*)
14	3-$NO_2C_6H_4$ (**6n**)	C_6H_5 (**7a**)	99 (**8na**)	81 (*S*)
15	2-$NO_2C_6H_4$ (6**o**)	C_6H_5 (**7a**)	85 (**8oa**)	85 (*S*)
16	1-naphthalene (**6p**)	C_6H_5 (**7a**)	95 (**8pa**)	90 (*S*)
17	2-furanyl (**6q**)	C_6H_5 (**7a**)	99 (**8qa**)	80 (*S*)
18	thiophen-2-yl (**6r**)	C_6H_5 (**7a**)	87 (**8ra**)	83 (*S*)

[a] See the Supporting Information for details. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] The absolute configurations were determined by comparing the optical rotation with those of known data.

Encouraged by the above results, we then studied the substrates of a variety of arylboronic acids **7b**−**h** that were subjected to the reactions with *N*-tosylimines **6** under the standard conditions. The results are summarized in Table 3. The corresponding diarylmethylamide products **8** were produced in good to excellent yields (80−99%) and ee's (85−93%), whether they have electron-donating or electron-withdrawing substituents on their benzene rings (Table 3, entries 1−7). Very recently, Ellman reported an efficient asymmetric addition of arylboronic acids to aliphatic *N*-tosylimines with Rh(I)/(*R*,*R*)-1-benzyl-3,4-bis(diphenylphosphino)pyrrolidine [(*R*,*R*)-Deguphos] catalytic system and showed great success.[10] To our delight, by using cationic Pd^{2+} diaquo complex **5b** as the catalyst, *N*-tosyl aliphatic imine substrates **6s** and **6u** led to products **8ue** and **8uh** in 80% yield/94% ee and in 65% yield/94% ee, respectively (Table 3, entries 11 and 12). Even for the linear *N*-tosyl

(10) For Rh(I)-catalyzed addition of arylboronic acids with *N*-tosyl and *N*-Dpp aliphatic imines, see: Trincado, M.; Ellman, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5623.

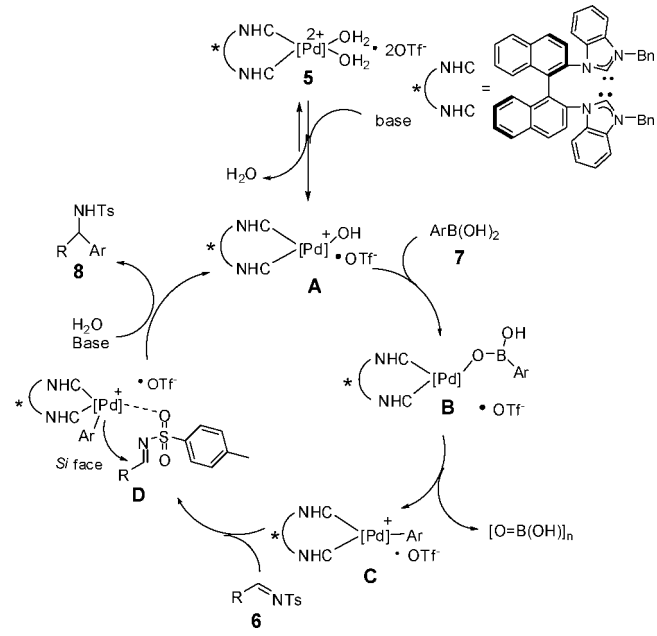
Table 3. Catalytic Asymmetric Arylation of *N*-Tosylimines **6** with Arylboronic Acids **7**[a]



entry	R	Ar	yield of **8**[b] (%)	ee of **8**[c,d] (%)
1	4-ClC_6H_4 (**6a**)	4-$CH_3OC_6H_4$ (**7b**)	90 (**8ab**)	84 (*S*)
2	4-ClC_6H_4 (**6a**)	3-$CH_3C_6H_4$ (**7c**)	92 (**8ac**)	84 (*S*)
3	C_6H_5 (**6t**)	4-FC_6H_4 (**7d**)	90 (**8td**)	81 (*R*)
4	C_6H_5 (**6t**)	4-PhC_6H_4 (**7e**)	80 (**8te**)	93 (*S*)
5	2-ClC_6H_4 (**6c**)	4-$CF_3C_6H_4$ (**7f**)	99 (**8cf**)	86 (*S*)
6	2-ClC_6H_4 (**6c**)	3-ClC_6H_4 (**7g**)	99 (**8cg**)	91 (*S*)
7	1-naphthyl (**6p**)	2-naphthyl (**7h**)	92 (**8ph**)	91 (*S*)
8	1-naphthyl (**6p**)	4-PhC_6H_4 (**7e**)	95 (**8pe**)	90 (*S*)
9	$CH_3CH_2CH_2$ (**6s**)	C_6H_5 (**7a**)	64 (**8sa**)	66 (*S*)
10	cyclohexyl (**6u**)	C_6H_5 (**7a**)	99 (**8ua**)	85 (*S*)
11	cyclohexyl (**6u**)	4-PhC_6H_4 (**7e**)	80 (**8ue**)	94 (*S*)
12	cyclohexyl (**6u**)	2-naphthyl (**7h**)	65 (**8uh**)	94 (*S*)

[a] See the Supporting Information for details. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] The absolute configurations were determined by comparing the optical rotation $[\alpha]_D$ with those known data.

Scheme 1. Proposed Mechanism for the Catalytic Asymmetric Arylation of *N*-Tosylimines with Phenylboronic Acid



aliphatic imine substrate **6s**, the corresponding adduct **8sa** was obtained in 64% yield and 66% ee (Table 3, entry 9).

A possible mechanism for this reaction is shown in Scheme 1. For the first step, the cationic NHC−Pd^{2+} diaquo complex **5** is converted into the Pd hydroxo complex **A** in the presence of base. Transmetalation of arylboronic acid **7** with palladium species **A** gives the corresponding palladium boronate complex **B**, which undergoes β-aryl elimination to result in the palladium−aryl complex **C**. The coordination of species **C** with the *N*-tosylimine **6** led to intermediate **D**. The addition of the aryl group to the imine from the *Si*-face furnishes the formation of adduct **8** upon hydrolysis in a highly stereoselective manner and regenerates the active species **A** to continue the catalytic cycle.[11,12]

In conclusion, we have successfully established new, efficient, chiral C_2-symmetric cationic NHC−Pd^{2+} diaquo complex catalysts and a catalytic system for enantioselective arylation of *N*-tosyl imines with arylboronic acids. This mild system provides easy access to chiral diarylmethylamides **8** in excellent yields and good to high enantioselectivities. The reactions showed a broad substrate scope which enables the use of a variety of *N*-tosylimines and arylboronic acids. Further optimizing this new catalytic system and probing the detailed mechanism is in progress in our group.

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Supporting Information Available: Experimental procedures, spectral and analytic data for **4a**−**e**, **5a**−**e**, and **8**, and X-ray crystal data of **5a** as well as chiral HPLC traces of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For directly observed transmetalation from boron to rhodium, see: Zhao, P.; Incarvito, D. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 1876.

(12) The formation of the key species **B** and **C** has been confirmed by ^{19}F NMR and ESI-Mass spectroscopic data (see the Supporting Information).